Managing Insidious Chemical Hazards and Vulnerabilities

Presented by

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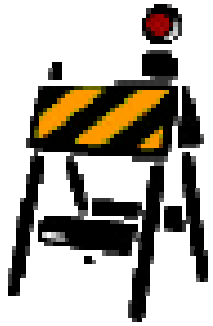
Gerlach Training & Consulting

Logistics

- **Emergency exits**
- **Restrooms**
- **Shelters**
- **Questions**
- **Break**
- **Beepers**

OBJECTIVES

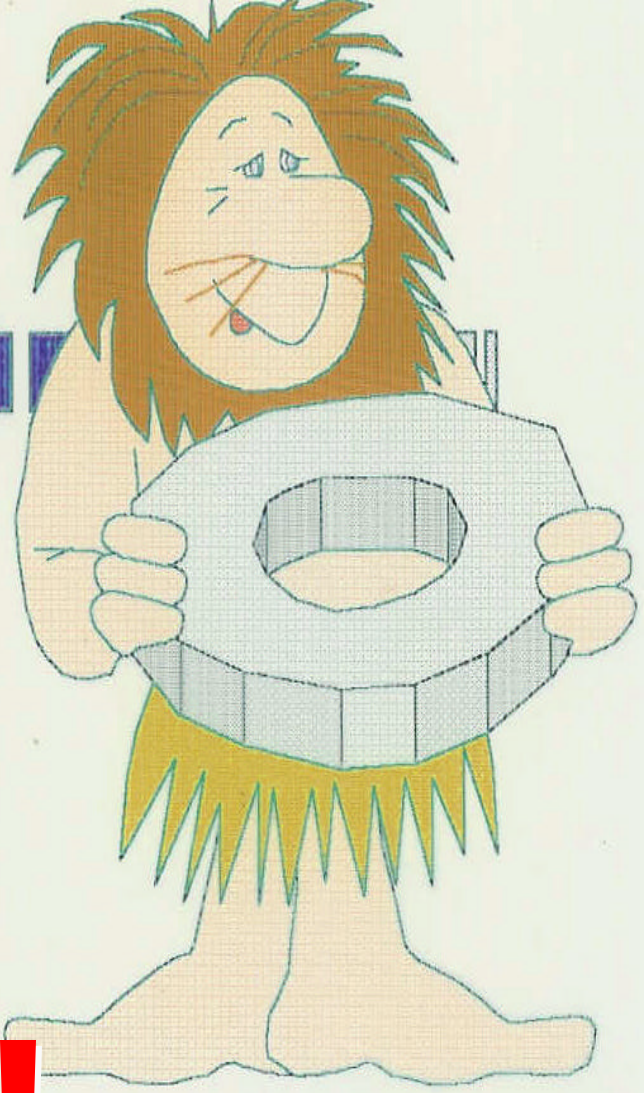


- Promote the need for hazard recognition
- To increase ability to recognize hazards
- Provide encouragement to take action once hazards are recognized

"The unrecognized and uncontrolled hazard presents the problem, not the existence of the hazard."

Derogazarian

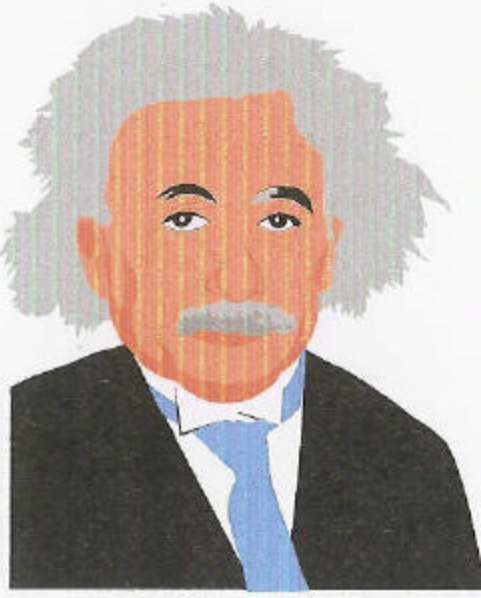
"Knowledge is power------



When applied !

"It's not how much you know--
It's what you do with what
you know"

A. Einstein




THINK SAFETY


Think Safety !
Act Safely !!!

Agenda
Two-Day Course

❶ "Responsibility to Act" video and discussion

❷ Basic Chemistry Concepts and Practices

❸ Hazard Communication Standard

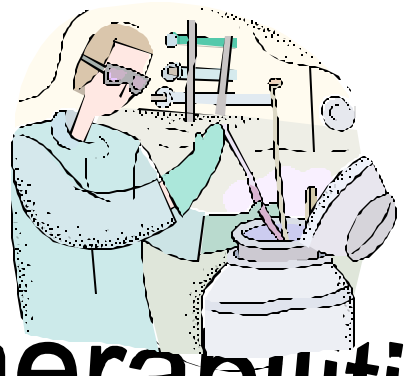
❹ Flammable Chemical Safety (discussion and demonstrations)

❺ Insidious Hazards

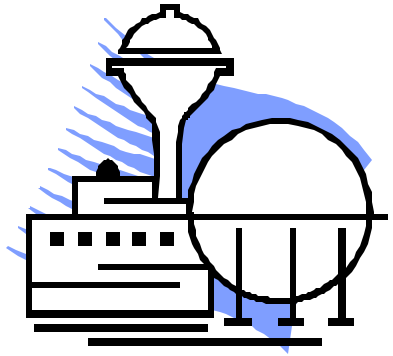
❻ Exercise (scenario –ID safety vulnerabilities)

❼ Corrosive Chemical Safety Discussion & demonstrations

8. Toxic Chemical Safety
9. Toxic Chemical Monitoring
10. Compressed Gas Safety
11. Storage Vulnerabilities
12. Handling Hazardous Waste Vulnerabilities
13. Sources of Information
14. Exercise Scenario- ID Chemical Vulnerabilities by Photo Analysis



Managing Chemical Vulnerabilities



A Reminder !

"The unrecognized and uncontrolled hazard causes the injury, not existence of the hazard."

What Do We Need To Know To Achieve Objectives?

- How many chemicals are known to humankind?

  About 30,000,000 with 1500 more each week

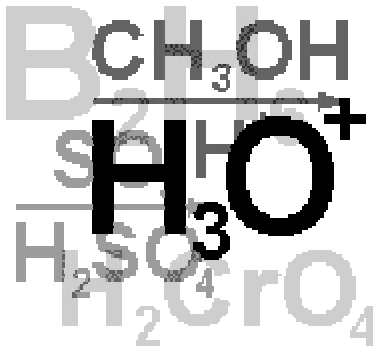
- What do we need to know about them?
  - Will it explode?
  - Will it decompose violently?

- Is it dangerous when involved in a leak, spill or fire?

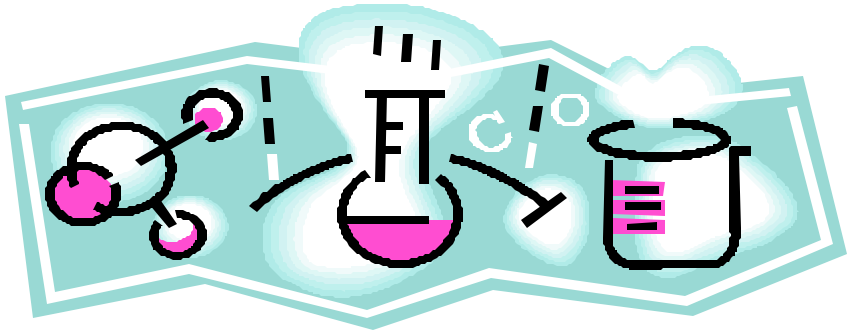
- Will it poison you? Are you likely to die if the chemical gets into your system? What are the possible routes of entry?
- Will it destroy tissue? Is it corrosive? Will its vapors irritate your eyes, nose, or throat?

- Will it polymerize violently?
- Is it susceptible to explosion by shock because of increased temperature?
- Will it give off toxic products of combustion?
- Will it give off toxic products of decomposition? (Even if not flammable)
- Will it violently react with extinguishing agents, (water, foam, dry chemical, carbon dioxide, etc.)

- Will it ignite spontaneously? Is it pyrophoric?
- Will it create an explosive mixture in air? Will it burn?
- Will it cause fire or explosion if it comes in contact with ordinary combustible materials?
- Will moisture cause it to ignite?

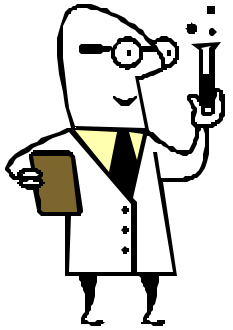


Basic Chemistry:
Concepts and Practices



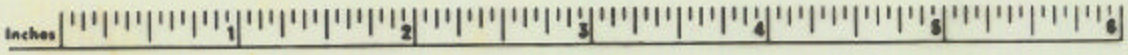
"Basic Chemistry" section of your book

Basic Chemistry: Concepts and Practices



Objectives

- "Refresh" (?) your memory on the periodic
- Review traits of the table that can be used to predict incompatibilities and vulnerabilities
- Acquaint you with certain chemical names that can be used to predict vulnerabilities



Allied Chemical

Periodic Chart of the Elements

IMPORTANT ATOMIC CONSTANTS

Avogadro's Number: (N_o) $(6.02257 \pm 0.00009) \times 10^{23}$ (g mole)$^{-1}$
Boltzmann Constant (k) $(1.38053 \pm 0.00006) \times 10^{-16}$ erg° K^{-1}
Planck's Constant (h) $(6.62554 \pm 0.00015) \times 10^{-27}$ erg-sec.
Gas Constant per mole (R, Nk) $(8.31432 \pm 0.00034) \times 10^{7}$ erg (g mole)$^{-1}$ °K^{-1}
Molar Volume (V_o) $(2.24136 \pm 0.00030) \times 10^{4}$ cm^3 mole^{-1}

IA	IIA	IIIB	IVB	VB	VIB		VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	INERT GASES
1 H 1.008																1 H 1.008	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.179
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.085	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.941	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.70	29 Cu 63.546	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (97)	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.868	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.30
55 Cs 132.905	56 Ba 137.33	57 La 138.905	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.2	83 Bi 208.980	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.025	89 Ac (227)															

58 Ce 140.12	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.4	63 Eu 151.96	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97
90 Th 232.038	91 Pa 231.036	92 U 238.029	93 Np 237.048	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (254)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

Numbers in ( ) parentheses are mass numbers of most stable isotope of the element

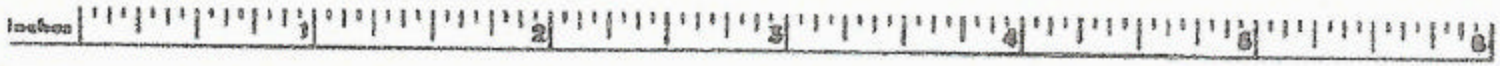
Periodic table

- Increasing atomic number ; (Z) =number protons
- Atomic number increases from left to right (periods)
- Atomic number increases from top to bottom (groups)
- Radius of atom decreases from left to right
- Radius of atom increases from top to bottom

Periodic table (2)

- *Atoms that tend to lose electrons are called METALS*
- *Atoms that tend to gain electrons are called* NON-METALS
- **As radius increases tendency to lose electrons increases; or tendency to gain electrons decreases.**
- **As radius decreases tendency to lose electrons decreases; or tendency to gain**

increases



Periodic Chart of the Elements

IMPORTANT ATOMIC CONSTANTS

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IA | IIA | IIIA | IVA | VA | VIA | VIIA | INERT GASES

1 H 1.008 | 2 He 4.003

10 Ne 20.179

18 Ar 39.948

36 Kr 83.80

54 Xe 131.30

86 Rn (222)

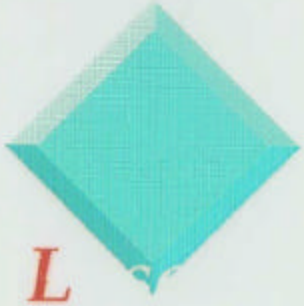
Metals= lose electrons

Non-metals Gain electrons

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
140.12	140.908	144.24	(145)	150.4	151.96	157.25	158.925	162.50	164.930	167.26	168.934	173.04	174.97

90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
232.038	231.036	238.029	237.048	(244)	(243)	(247)	(247)	(251)	(254)	(257)	(258)	(259)	(260)

Numbers in ( ) parenthesis are mass numbers of most stable isotope of the element



Periodic table (3)

L
O
R
A

G
R
O
A

Periodic table (4)

- Strongest metals (ability to lose electrons) are located at left-bottom of table
- Strongest non-metals (ability to gain electrons) are located at top-right of table

☹ What is a "fire"?

☹ What is needed for a fire?

Periodic table (5)

☹ $C + O_2$ yields CO_2 + heat

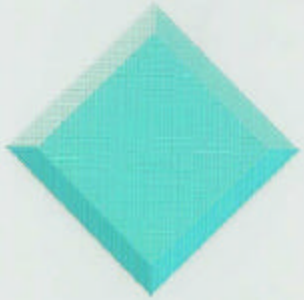
0 0 +4, -2

Carbon has lost electrons, i.e., oxidized

Oxygen has gained electrons, i.e., reduced

☺ Fe + O_2 yields Fe_2O_3 + heat

Fe from O to +3, i.e., Fe is oxidized



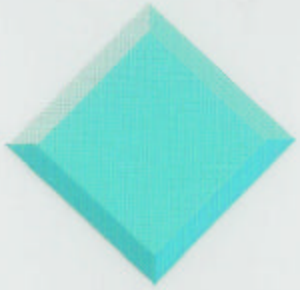
Periodic table (6)

- $Fe + Cl_2$ yields $FeCl_3$ + heat

  0 0 +3, -1

  Cl has gained electrons, i.e., is oxidizing agent

  Cl is oxidizing agent but has no oxygen !)



Reaction trends

Trends with water

- **Down Gp. IA**

  M + HOH yields MOH + H_2 (vigorous)

  (OE Weekly Summary 99-15, Li accident)

- **Across from left to right**

  Na is vigorous

  Mg forms hydrogen bubbles slowly

  Be needs steam

  Zn needs high temperature steam

Trends(2)

Trends with oxygen

- **Gp. IA**

  $2M + O_2$ yields metal oxides and or metal peroxides (OE wkly. summary 98-09, $K_2 O_2$)

- **Across left to right**

  Reaction goes from rapid to as exciting as "watching your car rust"

Trends (3)

- **Reaction with nitrogen**

$3\ Li + \frac{1}{2}\ N_2 \rightarrow Li_3N$ (Li only)

Explosive with heat or/and mechanical agitation

Trends (4)

- **Transition Elements**

Groups IIIA to IIB

These elements can have more than one valence (charge) in compounds. Therefore, their compounds can act as oxidizing agents.

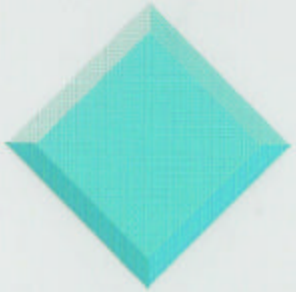
Group VIIB

Very corrosive because strong oxidizing agents can react violently with metals.

What's in a Name?
Prefix and Suffix Clues

An indication about a chemical's instability or tendency to react violently with other chemicals can often be obtained from:

- **The name**
- **Prefixes**
- **Suffixes**
- **Structure**



Names (partial list)

- **Any chemical name which contains any of the following probably is a strong oxidizer:**

Name fragment	Example
Nitrate	Ammonium nitrate
Nitrite	Sodium nitrite
Perchlorate (perchloric acid)	Lead perchlorate
Peroxide	Benzoyl peroxide

Names (2)
(partial list)

Chromate	Sodium chromate
Dichromate	Sodium dichromate
Picrates (picric acid)	Hg picrate
Permanganate	Potassium permanganate
Hypochlorite	Calcium hypochlorite
Chlorite	Sodium chlorite
Chlorate	potassium chlorate
Bromate	Calcium bromate

Structure and instability (partial list)

Compounds which contain any of the following features are prone to be unstable :

Compounds containing Carbon

Structural feature	Examples
C=C-C=C	Diene
C=C-C-=C	Alkenynes
C=C=C	Allenes

Structure and stability (2)

Compounds Containing Carbon and Nitrogen

C-N=N-C	Azo compounds
$C-N_3$	Alkyl, aryl azides
C-C-=N	Nitriles

Compounds containing Carbon and Oxygen

C-O-O-C	Diakyl peroxides
CO-O-O-CO	Diacyl peroxides

Compounds containing Carbon, Nitrogen, Oxygen

C-O-N=O	Alkyl nitrites
C=NOH	Oximes

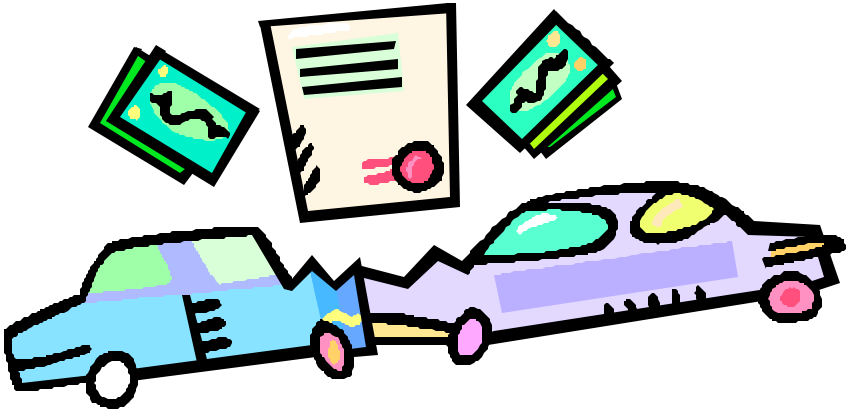
Structure and stabilities (3)

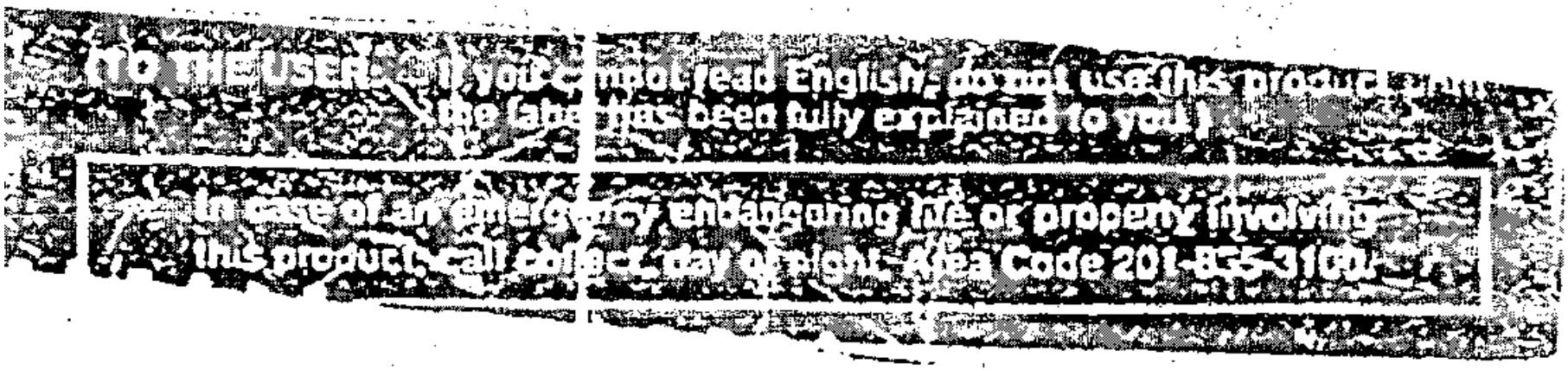
Compounds Containing Nitrogen and other Elements

N-X	**N-Halogen compounds**
N-metal	**N-heavy metal derivatives**

For a more complete listing see: "Improving Safety in the Chemical Laboratory", J. Young, ed., Wiley

Practical Quiz Time





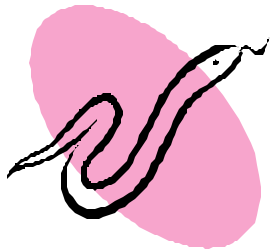
What is wrong with this label?

LABEL FOUND IN TEXAS:

(TO THE USER: If you cannot read English do not use this product until the label has been fully explained to you.)

In case of an emergency endangering life or property involving this product, call collect day or night. Area Code 201-835-3100

Insidious Hazards



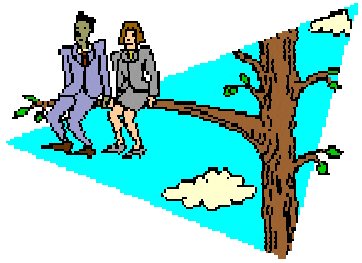
“A snake waiting to bite you”

“Working harmfully in a subtle manner”

“Lying in wait”

“Treacherous”

Human



- **Risk Perception**

- **We don’t all perceive risks the same. If don’t perceive a risk we are likely to do dumb things.**

INSIDIOUS

- **Conditions that represent potential hazard, and because we usually don’t, won’t, can’t see, hear, smell or taste them they are usually overlooked until they cause a near miss or an accident.**

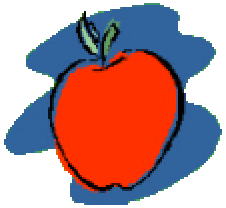
Wide Range of Possibilities

- Human
- Administrative
- Communications
- Physical
- Chemical

Risk perceptions

- Risk rankings (Science, Oct. 1988)
- Buxton, NC accident
- March Electric incident
- Manhole entry
- "Creative chemistry"

Risk Perceptions



Or

- **Which causes the greater risk of cancer: greater risk of Cancer?**
  - **(a) An apple with Alar**
  - **(b) 1 cup of coffee**

Answer: (b) Questionable science and 35,000 times a child's normal exposure

Buxton, N. C.

> >> > Buxton, NC: A man died on a beach when an 8-foot-deep hole he had dug> > into the sand caved in as he sat inside it. Beachgoers said Daniel> > Jones, 21, dug the hole for fun, or protection from the wind, and> > had been sitting in a beach chair at the bottom Thursday afternoon> > when it collapsed, burying him beneath 5 feet of sand. People on the> > beach, on the outer banks, used their hands and shovels, trying to> > claw their way to Jones, a resident of Woodbridge, VA, but could not> > reach him. It took rescue workers using heavy equipment almost an> > hour to free him while about 200 people looked on.> > Jones was pronounced dead at a hospital.> >> > In February, Santiago Alvarado, 24, was killed in Lompoc, CA, as he> > fell face-first through the ceiling of a bicycle shop he was> > burglarizing. Death

...if threatened or forced to defend property or dignity. Each person ... have quick and easy access to the

two countries is enormous—ann... the United States reports about ... times as many violent crimes per c... as does Japan. Apparently, if we b...

aper 12/22/94

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March workers evacuated after chemical reaction

STAFF REPORTS
THE DAILY JEFFERSONIAN

Twenty-one March Electric employees were sent to the hospital, examined and released after inhaling fumes from an apparent chemical reaction at the plant late Wednesday afternoon, an Ametek Inc. official said today.

According to Cambridge Fire Department reports, one worker was unconscious.

At 5:25 p.m. Wednesday, a March Electric maintenance worker accidentally pumped approximately 165 gallons of hot washer fluid from a tank into three old 55-gallon varnish drums, said Richard Sabol, corporate safety engineer.

Sabol said the hot washer fluid is non-hazardous and non-toxic.

Sabol said the temperature of the fluid, which was less than 180 degrees, created a vapor that smelled like glue and affected employees in the plant's bracket work area.

Employees complained of discomfort, including dizziness and upset stomach and were transported to Southeastern Ohio Regional Medical Center/Guernsey Memorial Hospital, where they were treated and released.

Firefighters arrived on the scene, evacuated the plant and removed the three drums. Sabol said the plant was ventilated and in about 80 minutes work resumed.

Those transported to the hospital went home after being released, plus about half of the remaining 100 workers decided to go home, said Sabol.

In the bracket area, brackets are placed in the hot solution for cleaning.

March Electric makes small motors for electrical equipment. 20000 rpm

"This solution is 98 percent water, which means you could take a bath in it. As a matter of fact, if you wanted to, you could drink it. But I wouldn't recommend it," said Sabol.

He said although the invesigation continued, it was believed the temperature of the water activated residual varnish left in the old drums.

According to various sources, the 120 workers evacuated from the plant stood outside in the chilly weather and then took refuge in the

Please see MARCH page 2

4. SHOCK-SENSITIVE CHEMICALS DISCOVERED IN WASTE DRUMS

On February 3, 2003, at the Savannah River Site, during sampling and characterization activities, workers found a 55-gallon drum that contained bottles of p-Dioxane, a chemical that can form explosive peroxide when exposed to air. (ORPS Report SR--WSRC-SLDHZD-2003-0002)

Workers were sampling drums of legacy waste bottles that had been shipped to the hazardous waste facility in 1985. Several bottles bore p-Dioxane labels in poor condition (Figure 4-1). However, the waste characterization form did not indicate that the drums contained p-Dioxane. When workers found the bottles labeled p-Dioxane, they stopped work. The contents of the bottles appeared to have crystallized.

An investigation revealed that a portion of the material inside the bottles was probably ice, as p-Dioxane freezes at 53° F (11.7° C). However, because the bottles had been in storage for such a long time, further evaluation will be needed to determine if peroxides have formed, and a hazardous waste vendor will test and stabilize the contents of the bottles.

HOW NOT TO ENTER A CONFINED SPACE

Manhole

BOOTH PHOTO - KRISTIN L. MILLER

HOLE IN ONE—The work-a-day world can be topsy-turvy, as Les Peters found out recently in West Branch. Peters, working for a company that is repaving a section of M-55 in the city's downtown area, was lowered through the manhole to see if the job was meeting specifications. Assisting were fellow workers John Lee, left, and Bob Trout, right.

Forklift Dual.jpg

A. Risk Rankings

Do Your Worries Match Those of the Experts?

Experts and lay people were asked to rank the risk of dying in any year from various activities and technologies. The experts' ranking closely matches known fatality statistics.

PUBLIC		EXPERTS
1	Nuclear Power	20
2	Motor Vehicles	1
3	Handguns	4
4	Smoking	2
5	Motorcycles	6
6	Alcoholic Beverages	3
7	General (Private) Aviation	12
8	Police Work	17
9	Pesticides	8
10	Surgery	5
11	Fire Fighting	18
12	Large Construction	13
13	Hunting	23
14	Spray Cans	26
15	Mountain Climbing	29
16	Bicycles	15
17	Commercial Aviation	16
18	Electric Power (Non-nuclear)	9
19	Swimming	10
20	Contraceptives	11
21	Skiing	30
22	X-Rays	7
23	High School & College Football	27
24	Railroads	19
25	Food Preservatives	14
26	Food Coloring	21
27	Power Mowers	28
28	Prescription Antibiotics	24
29	Home Appliances	22
30	Vaccinations	25

From *Science*, October 1988

Attitudes
Human

- **What attitudes can be insidious, or hazardous?**

✓ **"Can't happen to me"**

✓ **"Just this one time"**

✓ **" Always done it this way"**

✓ **"Safety people aren't here"**

✓ **Others**

"Don't come whining to me!
I told you not to pipet
by mouth."

Who has bad attitudes?
Human

- **Henrich Accident Study**

	CAUSE OF ACCIDENT	%
❶	Work conditions	10
❷	Worker activities	87
❸	Act of God	3

Who has attitude problems?
Human

- Met. Life Insurance study of the 87%

CAUSE OF ACCIDENT	%
❶ Physical & personal disability (vision, organic disease, worry)	20
❷ Due to attitude	67

0.67 x 87= 58% of accidents related to worker attitude

Who is Responsible for Worker Safety?

- **Over 95% believe workplace safety is the responsibility of:**

Answer: _____?

The Employer

"It can't happen to me"

"Just this one time"

Recognizing and removing insidious hazards can go a long way in reducing the probability of accidents

Pyrophoric compounds

- **React with air and its moisture so rapidly that the ensuing oxidation and/or hydrolysis leads to ignition.**
  - **Finely divided metals (Ca, Zr)**
  - **Metal hydrides or nonmetal hydrides (diethylaluminum hydride)**
  - **Carbonyl compounds (pentacarbonyliron)**

Unexpected explosives

- **Peroxidation**

  Compounds with autoxidizable hydrogen which reacts with atmospheric oxygen to form peroxides.

EXAMPLES

* **Methylene group adjacent to ethereal oxygen atom (-O-CH_2- as in diethyl ether, THF, dioxane)**

Further References

(1) “Improving Safety in the Chemistry Laboratory”, J. Young, ed., Wiley Interscience

(2) J. Chemical Education, 47, A175, (1970)

Chemical

- Vapors and gases

  Invisible, toxic, flammable, odor(?)

- Reaction with container

  Al + sodium arsenite yields arsine

- Azides, perclorates, picrates
  (salts of Pb, Cu, Hg, Au, Pd, Cd are explosive when dry) Includes picric acid

References

- **“Improving Safety in the Chemistry Laboratory”, J. Young, ed., Wiley Interscience**

Toxic by-products of accidental contact

Col. 1	Col. 2	Product
Arsenic compounds	A reducing agent	Arsine
Azides	Acids	Hydrogen azide
Cyanides	Acids	Hydrogen cyanide
Nitrates	Sulfuric acid	Oxides of nitrogen
Nitrites	Acids	Oxides of nitrogen
Phosphorus	Reducing agents or caustic alkalis	Phosphine

→ Extracted from: "Improving Safety In The Chemical Laboratory" J. A. Young, Ed.

Administrative

- Safety people lack full administrative support
- Equipment poorly maintained
- Safety equipment with dual function

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The EPA cautions that MSDSs from different sources for the same material may differ widely in their descriptions of hazards. They cite a comparison of four different MSDSs for the compound azinphos methyl. Hazard ratings for health/fire/reactivity were listed as 2/0/0, none listed, 3/2/2, and 4/0/0 in the MSDSs, where a higher number indicates a greater hazard. All four MSDSs also exhibited wide disparity in their narrative descriptions of reactivity hazards, incompatibilities, and fire hazards. For example, one MSDS described incompatibles as "acids and bases" while another described incompatibles as "heat, moisture." None of the MSDSs were entirely consistent with a Response Information Data Sheet developed by the National Oceanic and Atmospheric Administration and the EPA.

Recent Events
Lessons Learned Database

- LL-2003-LLNL-12

  Unattended Hotplate/stirrer Results in HF Spill

- LL-2003-LLNL-06

  Mixing Chemicals Can Lead to Storage Hazards (Sulfuric acid + potassium dichromate)

Lessons Learned database

- **Y-2003-OR-BJCETTP-0501**

  Missing Hazardous Waste Containing Cyanide

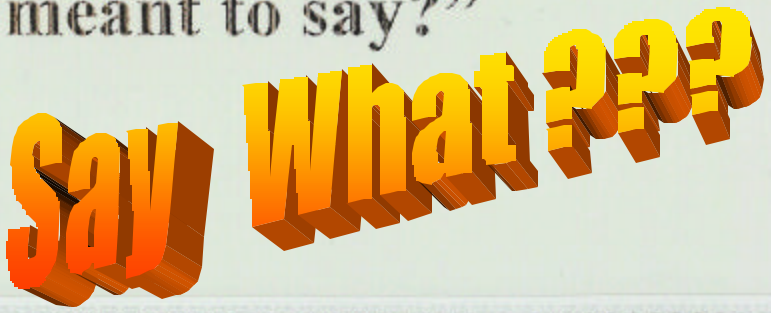
- **2003-SRS-WSRC-0008**

  Attempted Unauthorized Procurement of Chemicals

A Model of Clarity

A student comment

"If we know what we want to say and we say something, like from what we really want to say, but we know what we are talking about, but we just didn't write it down that way, will you know what I meant to say?"



The End !

Thanks for Your Attention